

taining more than 45% Cu. One possible explanation of this could be a change in the unknown transition probabilities which render such transitions less likely in copper-rich alloys. A more likely one is that the relative transfer of copper 4s electrons tends to decrease as the number of copper atoms increases. The retention of some 3d holes, even beyond the 60% Cu composition predicted by Mott, is supported by recent observations of the magnetic susceptibility of Cu-Ni alloys²⁰⁻²² and their electronic specific heats.^{23,24} A particularly in-

triguing suggestion, in view of the x-ray absorption spectra described above, is that due to an incipient miscibility gap in the copper-nickel system, there is a tendency toward segregation of nickel atoms in copper-rich alloys.²⁵ Since such clustering would minimize electron sharing between segregated copper and nickel atoms, it would serve to retain a number of 3d⁹ configurations in the alloy, thus explaining the x-ray absorption edges and the magnetic- and specific-heat measurements.

²⁰ E. P. Wohlfarth, Proc. Roy. Soc. (London) **A195**, 434 (1949).

²¹ K. Schröder, J. Appl. Phys. **32**, 880 (1961).

²² H. C. Van Elst, B. Lubach, and G. J. Van den Berg, Physica **28**, 1297 (1962).

²³ G. L. Guthrie, S. A. Friedberg, and J. E. Goldman, Phys. Rev. **113**, 45 (1959).

²⁴ K. P. Gupta, C. H. Cheng, and P. A. Beck, J. Phys. Radium **23**, 721 (1962); Phys. Rev. **133**, A203 (1964).

ACKNOWLEDGMENT

We would like to express our thanks to G. J. Klems for writing and testing the computer programs used to correct and normalize the data.

²⁵ F. M. Ryan, E. W. Pugh, and R. Smoluchowski, Phys. Rev. **116**, 1106 (1959).

Some Properties of a Double Acceptor Center in CdTe*

M. R. LORENZ,† B. SEGALL, AND H. H. WOODBURY

General Electric Research Laboratory, Schenectady, New York

(Received 9 December 1963)

When CdTe and other II-VI semiconducting compounds are heat treated with an excess of the cation component or are subjected to high-energy electron bombardment, a double acceptor is produced that has its second charged state close to the conduction band. The defect is characterized by its unique properties manifested in electrical transport and photoconductivity measurements. This paper deals with this imperfection in CdTe. It is shown that all of the observed properties associated with the defect are consistent with the double acceptor model. The energy of the doubly ionized state is 0.06 eV below the conduction-band minimum. In this state the defect is an effective hole trap at low temperatures. Electrons are strongly inhibited from recombining at the singly ionized center by an effective "barrier" of 0.27 eV. At moderately low temperatures ($T \lesssim 85^\circ\text{K}$), this phenomenon leads to marked departures from electronic equilibrium. On the basis of the preparative conditions leading to the center's production, it is suggested that the imperfection involves a native defect, most probably a vacancy, associated with a chemical impurity. Another defect with a level 0.6 eV below the conduction band, reported earlier by deNobel in heavily doped material, is found to be produced in samples fired under moderately low cadmium pressure. From the firing conditions and the Hall data it is inferred that this level is also due to an intrinsic imperfection.

INTRODUCTION

THE effects of departures from the ideal stoichiometric ratio on the electrical and optical properties of some compound semiconductors are well known. When these deviations are large relative to residual impurity concentrations, such as in the chalcogenides of lead¹ and tin,² certain induced properties can readily be ascribed to the created native defects. Most com-

pound semiconductors, however, have rather small shifts from the stoichiometric ratio. The magnitude of the deviation is often less than the residual impurity concentration so that the properties of native defects are obscured. In a broad survey of the properties of CdTe, deNobel³ studied the electrical behavior of *n*-type material as a function of impurity and stoichiometry. From his studies, he concluded that interstitial Cd atoms give rise to single-donor levels 0.02 eV below the conduction band. The concentration of this imperfection increased in direct proportion to the Cd pressure and could be sufficiently large under high P_{Cd} to dominate the electrical properties. However, in similar studies, Yamada⁴ was unsuccessful in attempts to obtain *n*-type CdTe by means of stoichiometric deviations.

* Supported by the Aerospace Research Laboratories, Office of Aerospace Research, U. S. Air Force.

† Presently at the Thomas J. Watson Research Center, IBM Corporation, Yorktown Heights, New York.

¹ R. F. Brebrick and R. S. Allgaier, J. Chem. Phys. **32**, 1826 (1960); J. Bloem and F. A. Kroeger, Z. Phys. Chem. (Frankfurt) **7**, 1 (1956); K. Igaki and N. Ohashi, Bull. Univ. Osaka Prefect. Ser. A **11**, 89 (1962).

² W. Albers, C. Haas, H. J. Vink, and J. D. Wasscher, J. Appl. Phys. Suppl. **32**, 2220 (1961); R. F. Brebrick, Phys. Chem. Solids **24**, 27 (1963).

³ D. deNobel, Philips Res. Rept. **14**, 361, 430 (1959).

⁴ S. Yamada, J. Phys. Soc. Japan **15**, 1940 (1960).

Recent electrical transport results on high-purity *n*-type CdTe⁵ strongly suggest that the earlier results were influenced by the presence of relatively high concentrations of foreign impurities. In fact, it has been shown that heat treatments of the higher purity material produced results⁶ which are in direct conflict with the earlier work³ on CdTe.

In this paper we will describe the characteristics of a center having the properties of a double acceptor that has its second charged state close to the conduction band. This imperfection occurs in other II-VI semiconducting compounds in addition to CdTe, the material to which we will restrict our attention in this paper. A double acceptor center can be created by means of the conventional heat treatment in Cd atmospheres and by electron bombardment. The electrical and some photoconductive properties of this defect were studied and will be discussed in detail. Annealing studies have also been carried out. Some conclusions on the identification of this center, which is believed to be a complex involving a native defect, are drawn from these observations and several alternative models are considered.

In addition, we will also briefly report on a much deeper state, 0.6 eV below the conduction band, which was observed earlier by deNobel.³ From the preparative conditions under which this level is observed in the present samples and from the electrical properties of these samples, we infer that it too is due to an intrinsic defect.

EXPERIMENTAL

High-purity CdTe was prepared by a technique already described.⁷ Hall samples, approximately 2.5×2.5×12 mm³, were cut from zone-refined ingots and carefully cleaned. The earlier method utilizing H₂SO₄ and K₂Cr₂O₇ chemical polishing solution⁸ was abandoned because it invariably left the samples lightly Cr doped.⁹ Instead we used the HF:HNO₃:2H₂O solution followed by a treatment in boiling 50% NaOH solution to remove any surface Te or its oxides. Samples were finally washed in dilute HCl and carefully rinsed. They were then sealed in small evacuated quartz ampoules with just sufficient Cd metal to establish the solid-liquid equilibrium at the heat treating temperature. For heat treatment as a function of Cd pressure at a fixed temperature, a two-compartment tube was used in a two-zone furnace. After firing, the sealed samples were quenched in silicone oil and electroded with minimum possible heating. Resistivity and Hall measurements

were made as a function of temperature by standard dc methods. There were provisions for irradiating the samples with a small incandescent lamp mounted inside the cryostat.

Samples for electron bombardment were cut down to 1.5×1.0×10 mm³. They were electroded and the resistivity and Hall coefficient were measured. Samples were then bombarded with 1.5-MeV electrons at room temperature for equal times on two opposite sides to obtain reasonably uniform damage throughout. Resistivities and Hall coefficients were remeasured. Annealing of bombarded samples was carried out at 300–350°C in an atmosphere of H₂. A first rough attempt at studying the effect of electron irradiation at low temperature was carried out. A sample immersed in liquid nitrogen was bombarded and then mounted in the Hall apparatus while cold. It is estimated that the sample never exceeded a temperature of 200°K during these operations.

The ionization and deionization of the 0.06-eV double acceptor level was investigated by means of photoconductivity. The dependence of the occupancy of this level on the photon energy was studied at 77°K by using a number of filters to isolate various ranges of wavelength.

RESULTS

When samples are fired at high temperatures, e.g., 900°C, very rapid changes take place. After surface removal, quenched samples show distinctly different bulk electrical properties than their original counterparts. These changes are not solely thermal since they are also influenced by changes in the Cd pressure. For example, the absence of Cd at the firing temperature results in the formation of *p*-type material. The changes produced by the firing are essentially complete within the time the sample reaches the firing temperature and are so rapid that it is questionable if the high-temperature atomic equilibrium state can be closely maintained during quenching to room temperature. Even at room temperature, increases in the resistivity of the quenched samples of about 10% per day, and occasionally more drastic changes, have been noted. These observations suggest that the results presented here depend strongly on quenching conditions, which, of course, are not very reproducible even when considerable care is exercised. Our samples were quenched and immediately stored at liquid N₂ temperature. They were slightly heated during electroding, reaching a maximum temperature of about 200°C for a few minutes. Possible changes in samples could also result from this additional heating. Thus, all results on quenched samples must be considered only as an indication of the high-temperature equilibrium. In contrast to the fired and quenched crystals, the irradiated samples showed relatively little change at 25°C. Also the original zone refined crystals were completely stable over periods of months.

Figures 1 and 2 give the carrier (electron) concentration (calculated from $(eR_H)^{-1}$ where R_H is the Hall

⁵ B. Segall, M. R. Lorenz, and R. E. Halsted, *Phys. Rev.* **129**, 2471 (1963).

⁶ M. R. Lorenz and H. H. Woodbury, *Phys. Rev. Letters* **10**, 215 (1963).

⁷ M. R. Lorenz and R. E. Halsted, *J. Electrochem. Soc.* **110**, 343 (1963).

⁸ T. Ichimiya, T. Niimi, K. Mizuma, O. Mikami, Y. Kamiya, and K. Ono, in *Solid State Physics in Electronics and Telecommunications*, edited by M. Desirant and J. L. Michiello (Academic Press Inc., New York, 1960), Vol. 2, p. 845.

⁹ G. W. Ludwig and M. R. Lorenz, *Phys. Rev.* **131**, 601 (1963).

coefficient and e is the electron charge) and the Hall mobility μ_H as a function of temperature for typical samples. The curves marked A are for a sample cut from a zone refined ingot, i.e., a sample characteristic of slowly cooled material. The behavior of the same sample after being fired in excess Cd for three minutes at 900°C and then quenched is exhibited by the curves B. These curves are typical of those corresponding to samples fired for times ranging from a few minutes to 30 minutes. Each set of data consists of two curves; the solid curve corresponds to measurements in the dark and the dotted curve to the same measurements after photoexcitation at the lowest temperature.

The sharp decrease in carriers starting at approximately 160°K as shown by the solid line of set B, Fig. 1, indicates the freeze-out of mobile electrons into a level about 0.06 eV below the conduction band. Around 110°K the electronic equilibrium starts to lag the thermal equilibrium. With decreasing temperature, this lag increases until at about 85°K it requires several hours to establish electronic equilibrium. At lower temperatures it becomes practically impossible to reach equilibrium with regard to the 0.06-eV level. The corresponding sluggish behavior was observed when the temperature was raised through this critical temperature range.

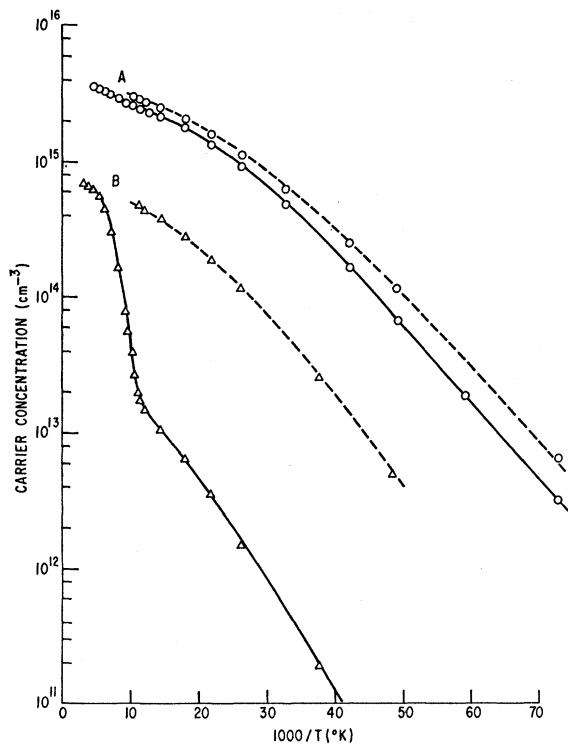


Fig. 1. Typical electron concentrations as a function of temperature. Curves A correspond to a zone-refined sample and B to the same sample quenched after being heated at 900°C in a saturated Cd atmosphere for three minutes. The solid curves represent measurements in the dark and the dashed curves measurements after photoexcitation at low temperatures.

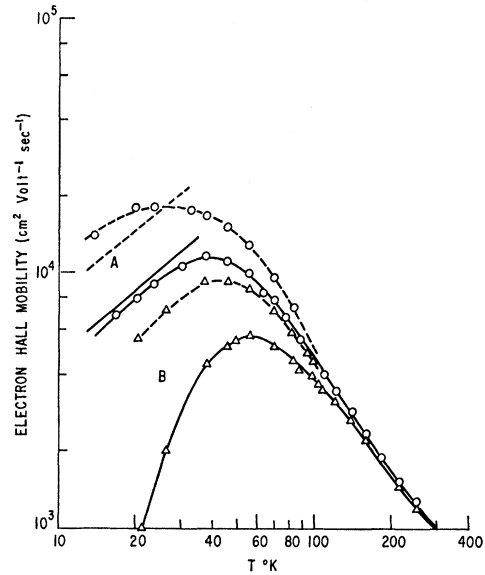


Fig. 2. Electron Hall mobilities for samples shown in Fig. 1. The solid and dashed curves have the same significance as in Fig. 1. The small segments at low temperature are calculated results for the zone-refined sample.

When such a sample is irradiated with light from an incandescent lamp in the cryostat at or below liquid N₂ temperatures, a sharp increase in the concentration of conduction electrons is noted. Simultaneously, the mobility shows a marked increase as illustrated in Fig. 2. These higher electron concentrations and mobilities persist even when the light is turned off and no measurable change could be detected after many hours. On warming the sample a sharp decrease in carriers is noted as the temperature reaches the critical region, i.e., approximately 100°K. The mobility shows a corresponding decrease to its "dark" value. At this point electronic equilibrium is re-established.

The above characteristic behavior suggests that some sort of barrier is associated with the center. The decay of conduction electrons following photoexcitation was measured at four temperatures in the critical region, i.e., 95 to 115°K. For samples whose behavior is similar to that represented by the curves of set A in Fig. 1, the simple relation $\Delta n = n - n(\text{equil}) = c \exp(-t/\tau)$ was observed over three decades of Δn at each temperature, and over the limited temperature region the lifetime can be expressed as $\tau = \tau_0 \exp(0.27 \text{ eV}/kT)$ where $\tau_0 = 3.2 \times 10^{-12}$ sec. For samples similar to that associated with set B in Fig. 1 where the number of conduction electrons are much smaller than the number of unfilled centers belonging to the 0.06-eV level, the kinetics of the decay are much more complex. The above results are equivalent to those that would be produced by an impenetrable barrier of height 0.27 eV above the conduction band minimum.

Measurements of the photoconductivity versus photon energy indicated that band-gap and higher-energy

radiation is most effective in emptying the 0.06-eV level. It is concluded that under these conditions the center acts as an effective hole trap (see discussion). Direct excitation of the center with photons between 0.3 and 1.0 eV has also been observed. However, the photoconductive cross section at these energies is several orders of magnitude lower than with band gap radiation. In addition, when the long-wavelength irradiation followed illumination by light of $h\nu > E_g$ a slow decrease in the conductivity was observed.

Changes produced by varying the Cd pressure P_{Cd} at a fixed temperature are of significant interest in the study of native defects in this material. Typical of these results are the R_H curves shown in Fig. 3. These illustrate the differences between samples fired for 10 min at 900°C under various pressures and an unfired sample cut from the same crystal. The general trend of the lowering of the Fermi level with decreasing P_{Cd} is quite clear. With P_{Cd} about 1 atm, samples invariably showed a very sharp freeze-out of electrons into a level about 0.6-eV deep, while $P_{Cd} \rightarrow 0$ always produces p -type material. The apparently slightly contradictory behavior seen at intermediate pressures is an example of the difficulty encountered in dealing with fast kinetics as was discussed above.

As is evident from Fig. 3, the samples fired at $P_{Cd} = 2.2$ and 3.4 atm show a freeze out into a deep level at high

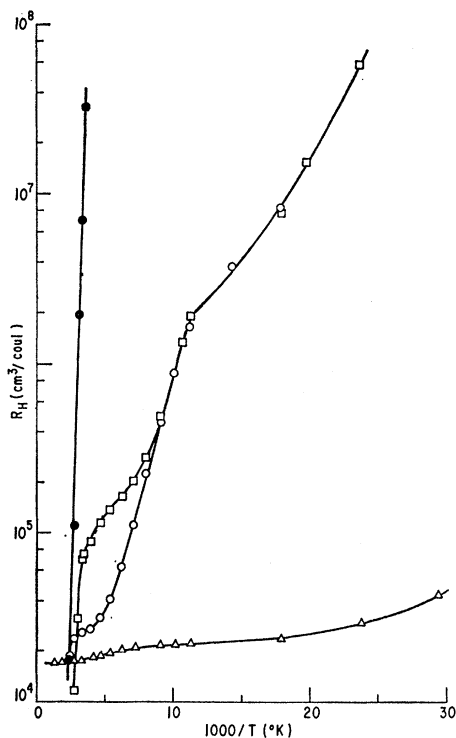


FIG. 3. Hall coefficients for samples fired at 900°C under the following Cd pressures: \square 3.4 atm, \circ 2.2 atm, \bullet 1.4 atm. The triangular symbols denote data from an unfired sample cut from the same crystal as the above.

temperature in addition to the 0.06-eV double-acceptor level. Presumably the deeper level is the same as the 0.6-eV level present in the samples fired at $P_{Cd} \approx 1$ atm. On the other hand, there is no measurable indication of this level in the original zone-refined material. It is thus quite evident that the 0.6-eV level is introduced during the firing. Other relevant information regarding this defect is that the mobilities measured in the sample fired at $P_{Cd} \approx 1$ atm were quite low being about 10^3 $\text{cm}^2/\text{V sec}$ at 300°K and rising roughly to the intrinsic μ_H value at about 400°K. It is very unlikely that these low μ_H values can be attributed to foreign impurities since it is very doubtful that a sufficiently high concentration ($\sim 10^{18} \text{ cm}^{-3}$) could diffuse into the crystals during firing times as short as 10 min. The most plausible interpretation of the data is that the imperfection in question involves a native defect. An optical absorption peak believed associated with transitions to the 0.6-eV level has been reported elsewhere.¹⁰ The determination of the electrical properties of this state is hindered by the fact that these properties are somewhat unstable in the temperature range in which such a deep level must be studied. Gradual changes occur at room temperature and marked changes take place fairly rapidly at 100°C or higher

deNobel⁸ had also observed the 0.6-eV level in In-doped samples which were equilibrated at low P_{Cd} . He assigned the level to the doubly charged state of the cadmium vacancy. However, according to a self-compensation model proposed by Mandel¹¹ it would be impossible to raise the Fermi level closer to the bottom of the conduction band than half the energy separation between the double ionized level of the compensating defect and the conduction band. Since n -type CdTe can be made degenerate,⁵ the assignment of the level to the doubly ionized state of an isolated cadmium vacancy is in conflict with Mandel's model. The latter does not preclude the possibility that the center is of more complex nature involving a cadmium vacancy. Our present results only indicate that a native defect is involved.

Bombardment of CdTe samples with 1.5-MeV electrons at 300°K leads to results rather similar to those produced by thermal treatment under Cd pressure. The Hall constants for a sample which was not highly purified are shown in Fig. 4. Results are presented for the sample before and after irradiation and after two stages of annealing. The corresponding Hall mobilities are given in Fig. 5. The results on the samples bombarded at low temperature (i.e., $T \lesssim 200^\circ\text{K}$) are entirely comparable to those bombarded at room temperature.

A saturation in the defect's production with bombardment is illustrated in Fig. 6 where R_H is shown for a sample of highest purity before and after several successive irradiations. The full curves are indicative of

¹⁰ M. R. Lorenz and B. Segall, Phys. Letters 7, 18 (1963).

¹¹ G. Mandel (to be published).

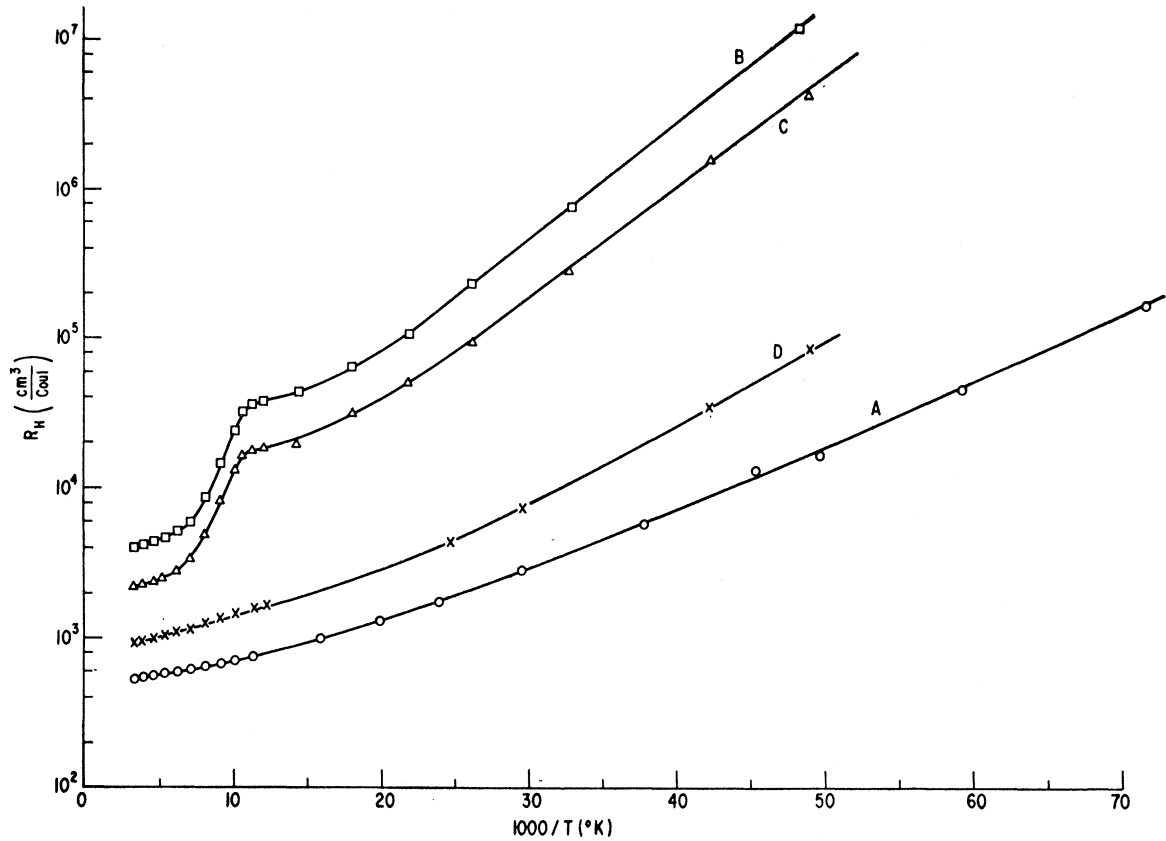


FIG. 4. The temperature dependence of the Hall coefficient of a sample before and after electron bombardment and after two stages of annealing. Curve A is for the original sample; B is for the sample after bombardment by 3×10^{16} 1.5-MeV electrons cm^{-2} on two opposite sides; C is for the sample after heating at 300°C for 15 min; and D after heating an additional 30 min at 350°C .

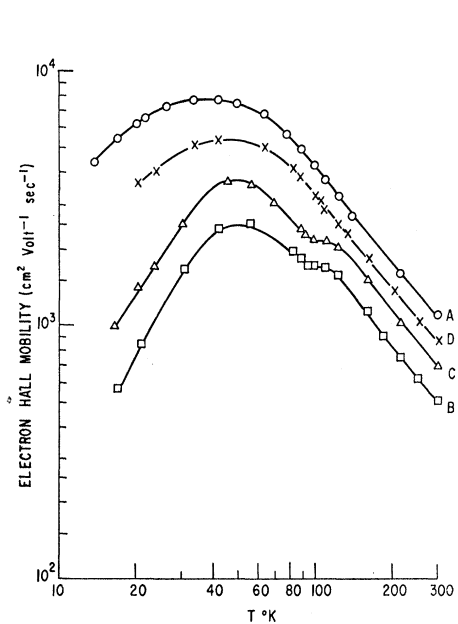


FIG. 5. The Hall mobilities corresponding to samples shown in Fig. 4. The symbols have the same significance as in Fig. 4.

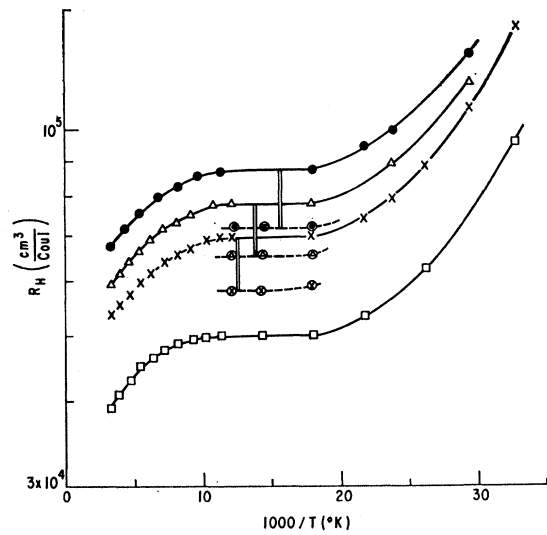


FIG. 6. The effect of varying dosages of electron irradiation on the Hall coefficient. The \square represents data on the unirradiated sample while \times , \triangle , and \bullet denotes data on the same sample after exposures of 8, 16, and 24 min to a 1.5-MeV beam of electrons. The solid and dashed curves have the same significance as those in Fig. 1.

the electrical behavior in the dark. The Hall effect in the critical temperature region after low-temperature photoexcitation is given by the short dashed sections of curves (kept short for purposes of clarity). From the difference of the two measurements the concentration of deionizable 0.06-eV centers can be calculated. For the sample shown here the saturated concentration was about 1.5×10^{13} centers/cm³ for the three doses of radiation.

ANALYSIS OF THE ELECTRICAL DATA

In the present section we will discuss the results of analyzing the electrical data presented in Figs. 1 and 2 and data on a number of similar samples. The approach employed was to assume that the 0.06-eV level is the second acceptor level of a double acceptor (A_2), whose detailed identity is not further specified. As will be seen, the consistency of the analysis supports the validity of the double acceptor assumption.

From a brief inspection of the data, as typified by the results in Fig. 1, it can be seen that a general analysis of the carrier concentrations should include the effect of both the double acceptor and the shallow, or hydrogenic, levels. The pictorial representation of the model is given in Fig. 7 where the notation D , A_2 , and A refer to the hydrogenic donors, double acceptors, and other compensating acceptors, respectively. Assuming the Fermi level is always above the first ionized state of the A_2 center, i.e., there are no neutral acceptors in the system, the charge neutrality condition for this system is:

$$\begin{aligned} N_{D^+} &= n + N_A + N_{A_2^-} + 2N_{A_2^{=}} \\ &= n + N_A + N_{A_2^-} + N_{A_2^{=}}, \end{aligned}$$

where $N_{A_2^-}$ and $N_{A_2^{=}}$ are the singly and doubly ionized states of the center and $N_{A_2} (= N_{A_2^-} + N_{A_2^{=}})$ is the total concentration. N_{D^+} , the concentration of ionized donors, is given by the usual expression. It is also possible to write down general expressions for the various states of ionization for the center without specifying its nature in detail. For all the cases that we will be concerned with (i.e., the Fermi level is well above the energy level of the singly charged center), the probability that the center is doubly occupied is

$$N_{A_2^{=}}/N_{A_2} \approx \{1 + g_{A_2} \exp(E_{A_2^-} - E_F/kT)\}^{-1}.$$

The value of factor g_{A_2} , the degeneracy factor, will be left unspecified initially.

From the above discussion and the fact that we will be dealing with nondegenerate carrier concentrations, the equation for the carrier concentration n can readily be shown to be

$$n + (N_A + 2N_{A_2} - N_D) - N_{A_2} N_c^{A_2} (N_c^{A_2} + n)^{-1} + n N_D (N_c^D + n)^{-1} = 0, \quad (1)$$

where

$$\begin{aligned} N_c^{A_2} &= g_{A_2} N_c \exp\{-E_{A_2}/kT\}, \\ N_c^D &= \frac{1}{2} N_c \exp\{-E_D/kT\}, \end{aligned}$$

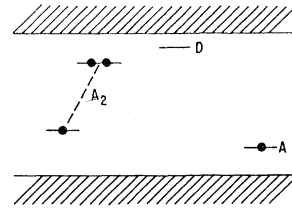


FIG. 7. Schematic representation of the defect levels controlling the electrical properties of CdTe containing the double acceptor center. The levels D and A represent the hydrogenic donors and compensating acceptors, respectively. The singly and doubly occupied double acceptor levels are indicated by A_2 .

N_c is the conduction-band density of states, and E_{A_2} and E_D here denote depths of the two levels below the conduction band. Under the appropriate conditions Eq. (1) goes over to the single level formulas for the shallow donors and the upper level of the double acceptor defect.

Several factors complicate the analysis. The first is that the acceptor level may be expected to be at least partially tied to the valence band, and as a result E_{A_2} may vary somewhat with T because of the variation of E_g .¹² However, since the important temperature range for the determination of E_{A_2} is rather small, the depth can be determined reasonably accurately at least in this range. The second complication is that for samples with an appreciable concentration of the double acceptor relative to, say, n at 300°K, the system goes out of electronic equilibrium at $T \lesssim 100^\circ\text{K}$. The analysis for these samples must therefore be restricted to a small range of T , thereby limiting the accuracy of the determined concentrations. The third complication concerns the degeneracy factor g_{A_2} . In order to specify a value we must have a more detailed knowledge of the imperfection. For one thing the value will depend on whether the center is an isolated native defect or is a more complex entity. Even in the former case it is not easy to determine its value. The most reasonable approach here would appear to be that employed by Teitler and Wallis¹³ in their discussion of multilevel acceptors in Ge. This approach, based on a localized tetrahedral bonding scheme involving the valence band states, leads to $g=4$ for the double acceptor level in question. However, it is doubtful that this value is correct in the present system since the state is so much closer to the conduction band than to the valence band that it is probably inappropriate to describe it entirely in terms of the valence band states. Furthermore the wave function for such a weakly bound state probably would not be sufficiently localized for their approach to be applicable.

The level depth can readily be obtained for the samples typified by curve A and curve B in Fig. 1. For the former we imply electronic equilibrium over the

¹² R. E. Halsted and B. Segall, Phys. Rev. Letters **10**, 392 (1963).

¹³ S. Teitler and R. F. Wallis, Phys. Chem. Solids **16**, 71 (1960).

full temperature range and we use the "step" in the carrier concentration and the fact that $N_{A_2^-}/N_{A_2} = (1+g_{A_2})^{-1}$ at the temperature for which $E_{A_2} = E_F$. The variation in the computed E_{A_2} arising from a reasonable range in the as yet unknown constant $g(\frac{1}{2}$ to 4) is only a few percent. Since the fired samples show a reasonable freeze-out (over two decades in some cases) before the time constant becomes prohibitively long, the depth can be obtained from a fit of n by the single level formula. Both methods lead to the consistent values, namely $E_{A_2} = 0.06$ eV.

In the zone refined samples where the concentration of the double acceptor is low, the carrier concentrations are sufficiently high to fill the 0.06-eV level before the samples are cooled through the critical temperature range. In this case the system is essentially in equilibrium and an analysis by the above equations is possible. In the low-temperature regions the carrier concentrations for the unilluminated and illuminated cases can be fitted by conventional single donor-level statistics. Reasonably unique values of N_D , N_A , and N_{A_2} are found along with a shallow donor depth which is consistent with the previous work on n -type CdTe.⁵ With these values (and minor adjustments) the fit of the two-level system is obtained. With consideration of the small contribution from deeper levels, which begin to manifest themselves at about 150°K, the fit is quite satisfactory.

The concentrations of charged defects obtained by the above analysis of the zone refined samples can be used to study the mobility and more specifically the increase in mobility brought about by the photoexcitation. It has previously been shown that the low temperature (15–40°K) mobility of these samples is determined by ionized impurity scattering.⁵ It is easily seen that the Debye screening length is the same for both the singly and doubly charged scatterers so that in the usual approximations (Brooks-Herring) the corresponding relaxation times for ionized impurity scattering from the doubly and singly charged centers are simply related by $\tau_2^{-1} = 4\tau_1^{-1}$. The hall mobility in the presence of N_1 singly and N_2 doubly charged scattering centers per cm³ for CdTe is then

$$\mu_H = \frac{1990T^{\frac{3}{2}}}{(N_1 + 4N_2) \times 10^{-15}} \times \frac{[\ln b(T) + 3.51]}{[\ln b(T) + 4.01]^2} \text{ cm}^2/\text{Vsec},$$

where $b(T) = 0.13T^2/n' \times 10^{-15}$ and $n' = n + N_D + N_D^0/N_D$. The calculated μ_H 's for the photoexcited and unilluminated cases, which are shown in Fig. 2 as the small segments of curves, are seen to be in good agreement, the magnitudes being in better agreement than might have been expected. The most significant aspect of the results is that the calculated difference is quite close to the observed difference in μ_H . It should be noted that comparable accord for $\Delta\mu_H$ has been found for the other zone refined samples which have been studied in detail.

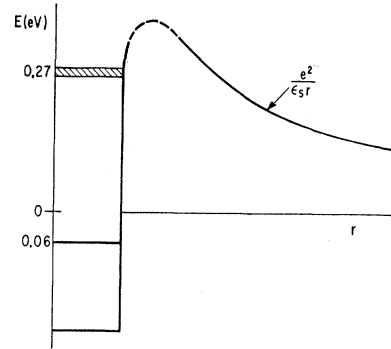


FIG. 8. Schematic representation of the potential energy of an electron in the presence of a singly occupied double acceptor center. The level at 0.06 eV below the conduction band represents the bound state while the broadened level at 0.27 eV represents a hypothesized quasibound state.

This quantitative agreement provides strong support for the proposed double acceptor nature of this center. The assumption that the defect is a triple acceptor and that the photoexcitation corresponds to a change in the charge state from -3 to -2 leads to appreciably smaller $\Delta\mu_H$'s than is observed.

A similar μ_H study for the fired samples is not practical since the T dependence of μ_H in these cases indicates that mobility is not simply determined by charged impurity scattering. The sharp decrease in μ_H with decreasing temperature (e.g., solid curve B in Fig. 2) suggests the onset of impurity banding. Analyses of n were carried out, however, to obtain estimates of the concentrations of defect produced by the Cd firings. For sample B the value $N_{A_2} \approx 3 \times 10^{15}$ has been determined; and comparable values were obtained for similarly fired samples. Another point of interest is that a consistent fitting of the light-on and light-off data could not be achieved with g_{A_2} appreciably different from 1. While this fact is not at present useful in itself, future detailed models of the center will have to be consistent with it.

BARRIER

In the previous section it was noted that below about 100°K electrons in the conduction band are strongly inhibited from freezing out into the 0.06-eV level. According to the double acceptor model this behavior is connected with the fact that in the singly occupied state the A_2 center is negatively charged and thus sets up a repulsive field for conduction electrons. It is the nature of the effective "barrier" which is associated with the repulsive field that we wish to consider here. In particular, we want to arrive at a qualitative understanding of the relation $\tau = \tau_0 \exp(E_B/kT)$, with $\tau_0 = 3.2 \times 10^{-12}$ sec and $E_B = 0.27$ eV.

It is useful to consider the potential that a conduction electron encounters. This is illustrated schematically in Fig. 8, and it is clear that three different regions ($r \gtrsim d$)

\equiv nearest-neighbor distance), $V(r)$ must be sufficiently attractive to bind the electron, and we represent it by a potential well. At large distances ($r \gtrsim a \equiv$ lattice constant) the field is the shielded Coulomb field $e^2/\epsilon_s r$, where ϵ_s is the static dielectric constant. The field in the intermediate region is unknown, although it is indicated by a dashed segment in Fig. 8. However, it is unlikely that the effective $V(r)$ would be very much larger than the shielded Coulomb value at $r \approx a$ because of correlations between the bound and conduction electrons.

In attempting a qualitative explanation we separate the probability of electron capture at the center into a factor giving the frequency with which an electron hits the center (or barrier) and a factor giving the probability that it goes over or through the barrier. Using $\tau_0 \approx [N\sigma v]^{-1}$ to approximate the former, where N corresponds to the number of centers ($\sim 10^{15} \text{ cm}^{-3}$), $\sigma = 4\pi r_0^2$ a cross section with r_0 roughly equal to 3 \AA and v an appropriate average velocity, we find the frequency factor τ_0 to be of the order of 10^{-9} sec. An estimate of the second factor was obtained by computing the WKB penetration factor $P = \exp[-\int_{r_1}^{r_2} |\kappa(x)| dx]$, where $\kappa(x)^2 = 2m^* \hbar^{-2} [V(x) - E]$ and r_1 and r_2 are the classical turning points. The essential result is that unless the effective potential is much larger than $e^2/\epsilon_s a$ in the "intermediate" region, the computed penetrability is very much higher than that which is required to explain the experimentally observed time constants. For example, if $V(r)$ is taken $= e^2/\epsilon_s a$ in the intermediate region, the average of P over the Boltzmann distribution for $T \approx 80^\circ$ is $\sim 10^{-4}$. If, on the other hand, the barrier is increased sufficiently to bring the P down to a more reasonable value for $T \lesssim 85^\circ$, the penetrability will be too low for $T \gtrsim 100^\circ$ where electrons reach equilibrium increasingly rapidly. In addition the T dependence will not be given correctly from the barrier penetrability alone.

One feature of the system which is characterized by the potential depicted in Fig. 8 is that the existence of the barrier produces a potential well with a "wall" at energies above the conduction band edge. We know that the well leads to a bound state (at 0.06 eV), and, in addition, that such wells lead to widely spaced discrete states. From consideration of the strength of the well required to bind the electron, and the boundary conditions on the wave function at the wall, it appears likely that there would be a quasibound or "virtual" level at a few tenths of a volt above the bound state. This "virtual" level would be expected to have an appreciable width due to a short escape lifetime.

The assumption of such a level at 0.27 eV above the conduction band could provide the explanation of the observed behavior. For those electrons in the Boltzmann distribution with $E < 0.27$ eV the amplitude of their wave function is sufficiently small at the center that capture is very improbable. At E around 0.27 eV, how-

ever, there is a resonance which corresponds to the quasi-bound state. For these energies the electron probability at the center, and thus capture probability, can become appreciable. When this resonance is averaged over the carrier distribution, it leads to the desired expression for τ with roughly the correct magnitudes.

We note that the observed and inferred double acceptor levels in the other II-VI compounds^{6,12,14} all have depths of roughly 0.1 eV, and that the $V(r)$ at fairly large r are nearly comparable. One would thus expect a similar τ and E_B in the other compounds. Aside from CdTe, the necessary studies have only been carried out in¹⁵ ZnSe for which a value of $E_B = 0.25$ eV was found.

PHOTOEXCITATION

The results of the photoexcitation experiments show that low-energy radiation (i.e., $h\nu < E_g$) is very much less effective in exciting the center than is band gap and higher energy radiation. This is readily explicable in terms of our double acceptor model. Photons of $h\nu \geq E_g$ are all absorbed within about one micron of the surface creating electron-hole pairs as well as excitons. Because of its charge, the doubly occupied center rapidly captures a hole, whereas the electrons are strongly inhibited from recombining at the A_2^- center because of the "barrier." Thus at low temperatures, essentially all of the A_2^- are rather quickly converted to the A_2^- state. At lower photon energies it is possible to excite the electrons directly from the center into the conduction band. However, because of the barrier, a minimum $h\nu$ of about 0.33 eV is expected for any significant excitation. The rate for this process is determined by the absorption constant α_{A_2} for the direct photodeionization of the center. Since α_{A_2} must be quite small for the concentration of doubly occupied center involved ($\sim 10^{15} \text{ cm}^{-3}$) it is seen that the photoexcitation for $h\nu < E_g$ must be relatively ineffective. To be able to calculate α_{A_2} in detail it is necessary to have more knowledge of the wave function for the center than is presently available. However, we have made rough estimates of this quantity using two simplified and somewhat complementary models¹⁶ for the center and find that $\alpha_{A_2} \sim 10^{-9} \alpha_B \sim 10^{-5} \text{ cm}^{-1}$, where α_B is the

¹⁴ M. R. Lorenz, M. Aven, and H. H. Woodbury, Phys. Rev. **132**, 143 (1963).

¹⁵ M. Aven, Air Force Cambridge Research Laboratories, contract No. AF 19(628)-329, Scientific Report No. 34, 1963 (unpublished).

¹⁶ The greatest uncertainty in estimating α_{A_2} arises from not knowing the fractions of conduction and valence-band states contained in the wave function ψ of the bound state. As one extreme model we assume that ψ can be expressed in terms of conduction band functions from around the band minimum. A significant reduction of α in this case results from the fact that ψ does not contain appreciable components of the relatively large wave vectors required for the transitions to conduction band states above the "barrier." In the other model we assume that the state can be represented by an expansion in terms of valence-band states with a nearly uniform expansion coefficient. This extreme model arises from the picture of the state as a very deep acceptor state.

average value of the absorption constant for band to band transitions. The estimate is in satisfactory accord with the equally rough experimental determination of 10^{-6} cm^{-1} for α_{A_2} .

The slow decrease in the conductivity observed when the long wave-length radiation is applied after high-energy irradiation is readily understood since the latter leaves essentially all the centers in the A_2^- state. The infrared photons then act to repopulate the 0.06-eV level by exciting the electrons "over the barrier."

The experiments indicate that "excitation" produced by band-gap light appears uniform throughout the bulk. Since the absorption takes place at the surface and the holes are expected to have fairly short lifetimes ($\tau \lesssim 10^{-8}$ sec),¹⁷ direct hole transport is probably not the chief mechanism. More likely mechanisms involve the transport of energy into the bulk by excitons or by the absorption and subsequent re-emission of radiation.

If the defect under consideration were a triple acceptor, one would expect it to be an effective hole trap at low temperatures in both its triply and doubly charged states. There was an absence of any photoeffect which could be associated with multiple trapping. This fact confirms the conclusion drawn from the analysis of the mobility data that the 0.06-eV level corresponds to a double acceptor level.

DISCUSSION

In the previous sections we have shown that all the experimental data relevant to the 0.06-eV level can be consistently interpreted only in terms of a double acceptor. The existence of the analogous defect level close to the conduction band in CdS⁶ and ZnSe^{14,15} demonstrates the general nature of the center. An interpretation of an important class of fluorescence emission found in several of the II-VI compounds in terms of the double acceptor level is also consistent with this observation.¹²

The fact that double acceptors exist in the II-VI compounds and that their second levels lie rather close to the conduction band deserves some comment.¹² The forces determining the position of the electronic level (and whether it exists in the gap at all) can be conveniently divided into the covalent forces tending to bind the electrons and the Coulomb repulsion between the electrons. Since the covalent tendencies are not expected to be very great (as compared, say, to those in Ge), the Coulomb interaction energy between the two electrons must be kept low. This condition is satisfied when the wave function for electrons is sufficiently diffuse so that the average interelectronic distance is fairly large and dielectric shielding becomes operative. The present results suggest that the covalent forces are sufficiently strong in the II-VI compound

family to give rise to a double acceptor level close to the conduction band.

It is interesting to compare the center under consideration with the double or triple acceptor impurity states found in Ge.¹⁸ Qualitatively, the observed changes in mobility and Hall coefficient with illumination correspond, for example, to those found in Mn-doped Ge. The important difference is that in Ge, electronic equilibrium is reached in short times (i.e., compared to those significant in the type of measurements considered here) even at very low temperatures. The fact that the electronic equilibrium is not maintained with regard to the 0.06-eV level in CdTe is understood in terms of the large barrier and the proximity of the level to the conduction band.

While it is not possible at the present time to definitively identify the double acceptor center, there are some general features of the center that can be inferred from the experimental results. The fact that a measurable concentration of the center can be produced either by a very short heat treatment or by a rather small dose of electron irradiation indicates that a native defect is involved. That the center does not occur in comparable concentrations in unquenched (and unirradiated) samples is also consistent with this conclusion. However, the fact that the concentration of the center appears to depend strongly on the purity of the sample suggests that the created native defects migrate to impurities with which they associate. The general model we propose is that isolated native defects are unstable (down to at least 200°K) but are stabilized when associated with chemical impurities.

The general picture of the center that we have drawn above is in line with the current knowledge of intrinsic point defects in other solids. The recent work on Si clearly indicates the instability of isolated vacancies in that material.¹⁹ Similarly the only intrinsic defect (V_{Zn}) identified in EPR studies of ZnS has always been found to be associated with impurities.²⁰ Investigations of the color centers in alkali-halides also illustrate the tendency of intrinsic defects, specifically the F center in the appropriate state of ionization, to migrate fairly readily and to associate with other defects.²¹ Apparently the vacancies in these materials, and probably most others, diffuse rapidly, and because of interactions such as the Coulomb attraction and strain relief readily associate with other defects.

Although the experimental information does not unambiguously tell us which of the four possible native

¹⁸ W. W. Tyler and H. H. Woodbury, Phys. Rev. **102**, 647 (1956).

¹⁹ G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. **31**, 86 (1961); G. D. Watkins, J. Phys. Soc. Japan **18**, 22 (1963).

²⁰ P. H. Kasai and Y. Otomo, Phys. Rev. Letters **7**, 17 (1961); A. Räuber and J. Schneider, Phys. Letters **3**, 230 (1963); J. Schneider, W. C. Holton, T. L. Estle, and A. Räuber, *ibid.* **5**, 312 (1963).

²¹ F. Luety, Z. Physik **165**, 17 (1961); N. Nishimaki, K. Kojima, and T. Kojima, J. Phys. Soc. Japan **16**, 576 (1961); H. Rabin, Phys. Rev. **129**, 129 (1963).

¹⁷ D. A. Cusano (to be published) has found a hole lifetime of $\sim 5 \times 10^{-10}$ sec in fairly highly In-doped ($\sim 10^{18} \text{ cm}^{-3}$) samples.

defects (cadmium and tellurium interstitials and vacancies) are involved in the A_2 center, some progress in the identification can be made from plausible physical and chemical considerations. First of all, there is no experimental evidence or theoretical basis for assuming that the Cd interstitial can act as an acceptor. The Te interstitial, on the other hand, would tend to have acceptor properties. However, its large ionic radius argues against its being an important defect and particularly against its being the mobile defect required. This leaves the vacancies, V_{Cd} and V_{Te} , as the most likely candidates. According to earlier covalent models of the native defects in compound semiconductors,²² the anion vacancy would act as a (double) donor. But we believe that these models are not sufficiently well founded to preclude an acceptor role for V_{Te} . In fact, we note that by extending the covalent bonding scheme that has been successfully employed in the interpretation of the EPR spectra of vacancies in Si¹⁹ to the present system, it can be seen that V_{Te} could act as a single or double acceptor.^{23,24} Also, it might be recalled that the analogous defect in the alkali halides, the F center, has a high-lying acceptor state (i.e., the F' center) in addition to its normal (donor) state.

The question of which of the two types of vacancies is involved is more difficult to decide. In principle, the trend in the production of the A_2 center by heat treat-

ment under various P_{Cd} would provide a means for deciding between the two. Unfortunately, the results of the firing experiments were too ambiguous, for reasons stated earlier, to settle this question.

At this stage of the investigations, we can at best speculate on the nature of the association and the identity of the specific impurity (or impurities) involved. We will merely mention a few possibilities. In the first, the native defect would tend to have two acceptor states in the forbidden gap and the association would be with an electrically neutral impurity (e.g., Zn at a Cd site or Se or O at a Te site, etc.). Such a complex would be analogous to the associated F center in KCl reported by Luety.²¹ As mentioned above, the role of neutral atoms might be to reduce the strain energy. A second possibility is that an intrinsic defect similar to one described above might associate with an (ionized) donor because of the Coulomb attraction. Other possibilities, perhaps more complex, might equally well explain the experimental observations. The only restriction to a complex center is that it behaves as a double acceptor. In conclusion we wish to re-emphasize that while a number of general features of the center have emerged, the detailed identification of the center remains unknown.

ACKNOWLEDGMENT

The authors wish to thank Dr. D. T. F. Marple for his generous cooperation with the photoconductivity experiments. They acknowledge L. H. Esmann's assistance in the experimental effort and Miss Elise Kreiger's help with the numerical analysis. They also wish to thank their colleagues for stimulating discussions.

²² See, for example, F. A. Kroeger and H. J. Vink, *Solid State Phys.* **3**, 307 (1956).

²³ This scheme would be appropriate if CdTe (and other II-VI compounds showing similar effects) has sufficiently covalent character so that the cations surrounding the V_{Te} will tend to pair off with a double bond between each pair.

²⁴ That V_{Te} could act as an acceptor does not preclude the possibility that it has donor levels below the acceptor state.